

CHAPTER - I

INTRODUCTION

1.1 INTRODUCTION

Since the pioneering researches of H. Staudinger in the 1920's, the science and technology of polymers have continued to advance, in tune with the ever increasing global demand for application-oriented materials. The synthesis and polymerization of structurally novel monomer systems are yet being continued in the polymer chemist's laboratory. However, at the same time, the possibility of chemical modification of existing polymer systems has opened up a new flood-gate of avenues, whereby the scope of the conventional polymer systems is enhanced to meet at least partly, the continuous demand for new materials.

Of the many variations of chemical techniques available and conceivable to modify polymer systems, a special status has been achieved by the concept of chemically modifying polymer systems by metal ion incorporation. Research on metal containing polymers started sporadically in the late 1960s, when several

workers found that vinyl ferrocene and other vinylic transition metal π -complexes would undergo polymerization under the same conditions as conventional organic monomers to form high polymers which incorporated a potentially reactive metal as an integral part of the polymer structure. It was gradually discovered that these metal modified polymer systems could have many desirable bulk properties such as modified dielectric, conductivity and thermal stability characteristics and the like. These potentialities were the reasons behind an explosive research emphasis during the 80's and 90's on metal containing polymer systems to explore new and novel application routes for these materials.

The work embodied in this thesis is directly concerned with the preparation and evaluation of metal containing polymers. A perusal of the research on metal containing polymers in the global context [J.E. Sheats, E. Carraher Jr., C.U. Pittman in 'Metal Containing Polymers', Plenum Press, N.Y. 1985] readily asserts that structure property co-relation warrants more concerted research efforts to understand the significance of metal-incorporation in polymer systems vis-a-vis its effect in monitoring the properties of these materials.

The work presented in this dissertation is a humble approach in the above mentioned direction. However, in order to identify the various objectives that motivated the present research, it would be helpful to be apprised of the present status of research in this field and the lacuna in these areas of research. Section 1.2 of this chapter is therefore devoted to a very brief survey on the present status on metal containing polymers which would be subsequently followed by a discussion of the objectives and scope of the present study.

1.2 PRESENT STATUS OF RESEARCH ON METAL CONTAINING POLYMERS

Research on metal-containing polymers started sporadically in the 1950s when Arimato and Haven¹ found vinyl ferrocene could be radically polymerized. The slow progress that continued from the 1960s gathered momentum gradually as evident from the frequent organization of national and international symposia in 1970, 1977-79, 1981, 1983, 1989 and 1992 which saw the field mature.

This section is intended to briefly highlight* the

A detailed version of the review has been published in Advances in Polymer Science, Biswas M, and Mukherjee A, Vol.115, 89-123(1994). See also Biswas M, Mukherjee A, Spl. issue, Frontiers in Macromolecular Science, Ind. J. Tech. Vol.31, 393-399 (1993).

significant developments in the field of metal-containing polymers during the last decade (1980-1991). The scope of this article will be restricted to the synthetic methodologies adopted and modification of physico-chemical properties of the various polymer systems with the incorporation of metal moieties in the skeleton. The procedures that have usually been adopted for introducing metal ions in the polymers may be conveniently discussed under the following headings: (1) Polymerization and copolymerization of metal-complexed monomeric moieties; (2) Anchoring of metal complexes on pre-formed polymers; (3) Metal loading by plasma polymerization (4) Doping and (5) Mechanochemical synthesis.

The application of these procedures will be discussed on the basis of selective examples from the various systems explored so far.

1.2.1 SYNTHETIC METHODOLOGIES

Polymerization and Copolymerization of Metal-complexed Monomeric Moieties

This procedure has been used in a limited number of

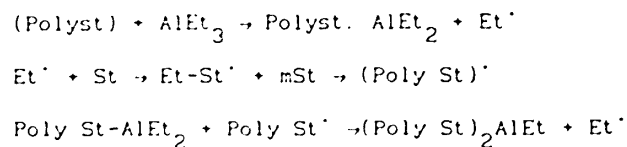
systems and suffers from the obvious disadvantage of the experimental complications involved. Usually, the metal ion is incorporated in the monomeric moiety followed by its polymerization.

Acrylic monomer systems

Acrylic monomer systems so far used in this context are monomers like iron methacrylate $[\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}]_3\text{Fe}$ and tributyltin methacrylate^{2,3}. They undergo free radical polymerization/copolymerization with other acrylates such as cyclohexyl, 2-ethoxyethyl, 2-hydroxyethyl and 2-hydroxypropyl. Synthesis of a metallo-macrocyclic acrylic monomer is illustrated by the reaction between a metallophthalocyanine tetracarbonyl chloride and 2-hydroxyethyl methacrylate (2-HEMA)⁴. Copolymerization of this monomer with N-vinylcarbazole (AIBN, benzene) results in a blue-green product soluble in usual solvents⁴.

Styrene monomer systems

A novel procedure⁵ is exemplified in the preparation of polystyryl aluminium derivatives by thermal polymerization of styrene in the presence of AlEt_3 acting as chain transfer agent.



Synthesis of a styrene monomer containing a diiron hexacarbonyl moiety and its copolymer together with the metal atom of the preferred copolymers has been achieved⁶. Synthesis of a typical cobalt chelated styrene derivative⁷ has also been reported.

Miscellaneous monomers

Polymer-bound dinitrogen complexes containing 'Mn' have been prepared⁸ directly from the polymer bound (η^5 -vinyl-methyl -cyclopentadienyl) tricarbonylmanganese (VCM) and molecular nitrogen in THF/benzene. The metal-containing base polymer may be rapidly prepared by AIBN initiated radical polymerization of the vinyl VCM with styrene or N-vinyl pyrrolidone.

Anchoring of Metal Complexes on Preformed Polymers

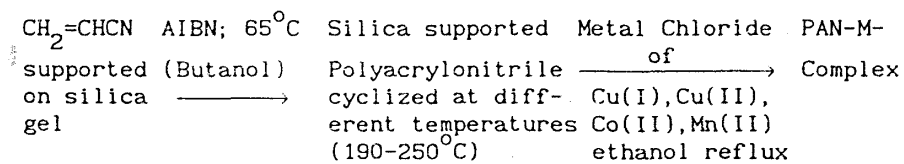
This appears to be the most widely adopted procedure for preparation of metal containing polymer systems.

Acrylic polymer systems

A Co(III)-Chelate⁹, bis-2-(2-azopyridyl)-1-naphthol Co(III) has been interacted with polyacrylic acid and other polyelectrolytes.

Metal specific ion-exchange resins bearing hydroxyoxime groups have been prepared¹⁰ from substituted phenylacrylates.

Silica supported cyclized polyacrylonitrile (PAN) metal complexes, claimed to be better oxidation catalysts than the polyphthalocyanine-metal complexes, have been obtained as shown below¹¹:



By an essentially similar procedure, silica-supported poly- (methacrylic acid)-palladium and platinum complexes have been obtained¹².

Copolymers of methacrylic acid and ethylene termed as 'ethylene ionomers' have been used as the base polymer for binding alkali, alkaline earth and transition metal

ions. Organic amines such as n-hexylamine, hexamethylene tetramine, 2,2,6,6-tetramethyl-4-hydroxy piperazine, ethylene diamine and polymeric diamines such as silicone diamine, polyether diamine and polymeric diamines such as silicone diamine, polyether diamine and polyamide oligomers considerably enhance the complex formation characteristics of Zn(II) ethylene ionomers thereby enhancing the physico-chemical properties¹³.

Styrene polymer systems

Polystyrene and its divinylbenzene cross-linked copolymer have been most widely exploited as the polymer support for anchoring metal complexes. A large variety of ligands containing N, P or S have been anchored on the polystyrene divinylbenzene matrix either by the bromination-lithiation pathway or by direct interaction of the ligand with Cl-, Br- or CN-methylated polystyrene-divinyl-benzene network¹⁴ (Figure 1.1).

In a novel procedure, chemical modification of uncross-linked atactic polystyrene by acetylation followed by a Claisen condensation with ethyl perfluoropropanoate has been used to prepare a macromolecular ligand bearing phenyl, perfluoroethyl,



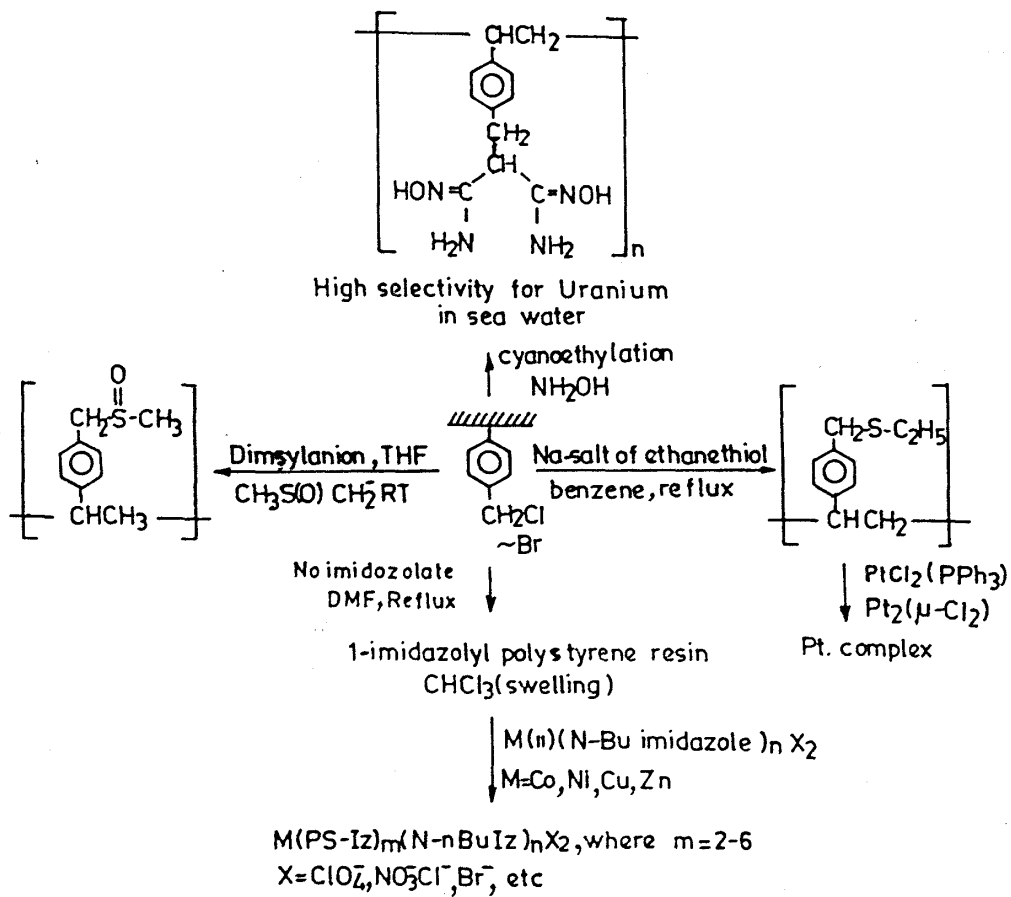


Figure 1.1 Polystyrene immobilized miscellaneous ligands.

1,3-diketone chelating groups, which readily form chelates with Cu(II), Ni(II) and Uranyl ions¹⁵.

The polystyrene-pendant $\text{Ru}(\text{bpy})_3^{2+}$ complex has been likewise obtained by the reaction of dichloro-bis(2-2'-bipyridyl-Ru(II)) complex with bipyridylated polystyrene¹⁶.

Coloured complexes of a number of 3d metal salts with dipyridylamine previously anchored on partially chloromethylated polystyrene-divinylbenzene matrix have been reported by Hendricker and Kratz¹⁷ and by Biswas and Mukherjee¹⁸.

A synthesis of much relevance is that of the copolymer (4-methyl,4'-vinyl 2,2' bipyridine/styrene)-pendant tris(2,2'- bipyridyl)ruthenium(II) complex as sensitizer for water photolysis with solar irradiation¹⁹.

2-Carboxybenzoyl and 1-carboxyl 8-naphthoyl partially substituted polystyrenes have been prepared by the Friedel Crafts reaction between polystyrene and the corresponding dicarboxylic anhydrides. Rare earth (Europium-III) complexes of these polymer based ligands have been obtained²⁰.

Miscellaneous ligands so far incorporated into the polystyrene matrix include imidazolyl²¹, 2-amido oxime²², thioether and sulfoxide moieties²³. The procedure is simple and essentially involves the halogen-replacement of Cl- or Br- from polystyrene matrix, bearing ~ CH₂Cl, or CH₂Br- groups. Mostly, first row transition element salts undergo facile complexation with these modified polystyrene matrices²¹.

A novel photostabilization process of anchoring ligands onto a polystyrene support which would eliminate the possibility of leaching the metal moieties by the coordinating solvent is due to Cais et al²⁴. A typical system is the phenanthrene chromium dicarbonyl moiety, anchored onto polystyrene support by a photochemical ligand substitution reaction in which one of the CO moieties would be replaced by a phosphino ligand covalently bound to the polymer²⁴. This would prevent the leaching of the Cr-moiety into the solution during a catalytic reaction in presence of the metallopolymer catalyst.

Saegusa et al²⁵ have developed a novel procedure of cationic grafting of phosphine oxide onto polystyrene. The 2-phenyl-1,2-oxaphospholane undergoes facile cationic

ring opening polymerization in presence of benzyl chloride. By analogy, a chloromethylated polystyrene (as the base polymer) readily yields a graft copolymer with a phosphineoxide graft chain with d.p. 4.7-10.5. This copolymer can be used as a chelating resin (bed type use) for UO_2^{2+} , Th^{4+} , Hg^{2+} , Pd^{2+} and Cu^{2+} to the extent of 80-100% depending on pH.

A novel cross-linking technique for localizing segments of polymeric chain molecules to give a three dimensional network structure displaying rubber like elasticity has been developed by Eichinger et al²⁶. An emulsion polymerized (isoprene-styrene/chloro-methylated styrene) copolymer on reaction with sodium salt of acetylacetonone (acac) undergoes controlled ligand complexation (1.4×10^{-4} mol/polymer g). Subsequent cross-linking by chelation of acac groups with palladium acetate affords a highly elastomeric network²⁶.

Heterocyclic polymer systems

Ru(II)-poly(4-vinylpyridine)²⁷, Ru(II)-poly(6-vinyl-2,2'-bipyridine)²⁸, Ru(II)-poly(4-methyl-4'-vinyl-2,2'-bipyridine)^{28,29}, Cu(II)-poly(4-vinyl-pyridine) cross-linked with 1,4-dibromobutane³⁰, Cr-complex

supported polyvinylpyridine resins³¹, Cu(II)-co-[(2-methyl-5-vinylpyridine)-acrylic acid]³² represent some of the widely studied systems as application-oriented materials.

Tsuchida et al³³, synthesized Poly(1-vinyl and 1-vinyl-2-methyl-imidazole) bound heme (iron-porphyrin) complexes as models for mimicking natural oxygen carriers such as hemoglobin. The reaction between AIBN polymerized poly(1-vinylimidazole, or poly(1-vinyl-2-methyl-imidazole) and Fe(III) protoporphyrin IX diethyl ester in DMF and small amount of $\text{Na}_2\text{S}_2\text{O}_4$ yields the Fe(III) complex.

N-Vinylpyrrolidone polymers are of special interest in medicine in the process of detoxification as well as for binding and removal of undesirable metallic ions and known as chelatotherapeutic agents³⁴. Free radical copolymers of poly(N-vinylpyrrolidone) and copolymers of N-vinylpyrrolidone and vinylacetate, vinylamine, vinylamidosuccinic acid are known to bind Cu^{2+} and other transition metal ions, and the resultant complexes exhibit interesting physico-chemical properties.

A polymeric ligand having pendant sulfide and imidazolyl groups binds Cu^{2+} to give an efficient oxidation catalyst³⁵. The base polymer is a free radical copolymer of ethylvinylsulfide and vinylimidazole.

Template Polymers

Template effects in chelating polymers constitute an interesting development in the field of metal containing polymers. The 'Template effects' are interpreted by the fact that the small molecule is templating a pattern in the macromolecule which can be recognized by the same molecule in a subsequent process. The idea is to prepare a polymer from the metal-chelated monomer, to remove the metal ion, and then to measure the selectivity of the prepared polymer for the metal ion of the template³⁶ (Figure 1.2). Typical examples of template systems are 4-vinyl-4'-methylbipyridine (Neckers³⁶) and 1-vinylimidazole (Tsuchida³⁷). These are polymerized in presence of divinylbenzene³⁶ and appropriate metal salts (Co^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+}). The template metal ions are removed by acid leaching and the polymer subsequently used for metal ion absorption studies.

Halogeno-telechelics

Halogeno-telechelic polymers result from complete ionization of both ends of telechelic prepolymers. Teyssie et al³⁸ developed a facile process of synthesizing dicarboxylato polymers based on Group IVb metal ions (Ti/Zr). Addition of a stoichiometric amount of tetra-n-butoxy-titanium $Ti(O-nBu)_4$ to a carefully dried 5% solution of a carboxy telechelic polybutadiene results in Ti-complex schematically shown in Fig.1.3. Halogeno-telechelic polyurethane-ureas have recently been synthesized from divalent metal salts (Mg^{2+} , Ca^{2+}) of p-amino-benzoic acid, diamine, dialkyl glycols and diisocyanates³⁹.

Miscellaneous polycondensates

Polyamides: Metallized plastics⁴⁰ have been obtained from metal chelates of nylon 4 and nylon 6 by soaking a film of the polyamides cast from formic acid/propanol mixture into a metal salt solution followed by reduction with $NaBH_4$. In this context, Huang et al⁴¹ developed an unique technique of 'retroplating out' in which activated metal plate (powder) surfaces are brought in contact for 5-10 seconds at room temperature with polyamide or

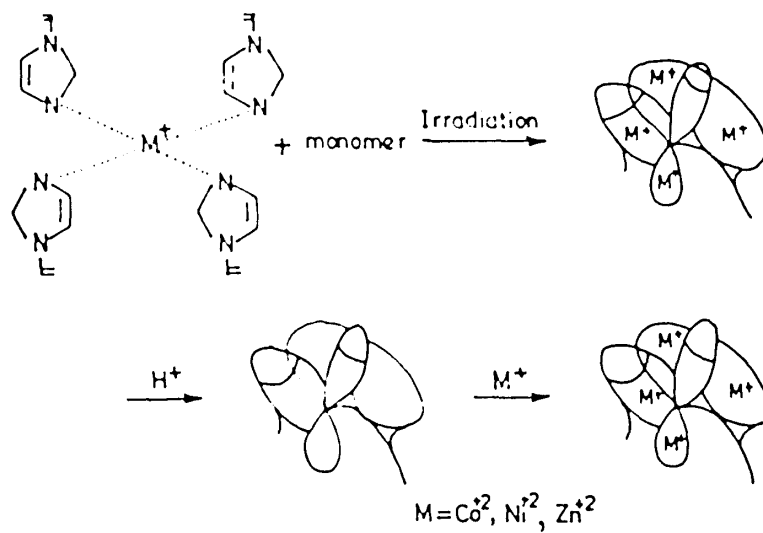


Figure 1.2 Template polymers.

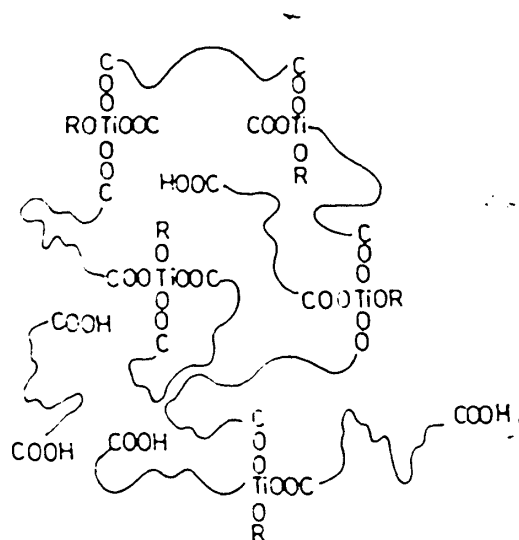


Figure 1.3 Halato-Telechelics

(polyvinyl-alcohol or polyacrylamide) metal chelate films to induce the retroplating out process.

Poly(amido-amine). Poly(amido-amine)⁴² offer a system to correlate the effect on Cu(II) complex forming ability with the number (n) of methylene groups between aminic nitrogen.

Polyimides. In situ co-deposition of metal salts such as Co(II), or LiCl into a polyimide precursor from 3,3', 4,4'-tetracarbo-xybenzophenone dianhydride and 4,4'-diaminobenzophenone with subsequent thermal curing offers surface-conductive polyimide film⁴³. By similar procedures, Taylor et al prepared a series of polyimides modified with Pd, Pt, Ag, Au, Cu, Sn and Ti magnetic-Fe^{44,45,46}.

In another set of reactions some methyl thiomethyl (MTM)-pendent polyimides⁴⁷ were allowed to react with bivalent ions of Ni, Zn, Cd and Hg and the metal ion uptake followed the order Hg (II) > Cd(II) > Zn(II) > Ni(II) respectively.

Polyurethanes. Metal-containing polyurethanes have been synthesized by polycondensing Co²⁺, Cu²⁺ salts of

mono(hydroxyethyl) phthalate with hexamethylene diisocyanate and tolylene diisocyanates⁴⁸.

Polycondensates with the Ligand as a Comonomer.

Metal-bearing polycondensates in which the ligand moiety alone or in combination with the coordinated metal ions form one of the backbone comonomers are exemplified by the following polymers reported by Wudl et al⁴⁹, Biswas and Mazumdar^{50,51} and by Takahashi et al⁵² in the synthesis of organotin polymer by a similar condensation process.

Poly(ethylene)oxide

Poly(ethylene)oxide-salt complexes have of late received considerable attention in view of their use as solid polymeric electrolytes. Complexes of PEO with LiBF_4 ⁵³, LiCF_3SO_3 ⁵³, modified with polydimethyl siloxane⁵⁴, LiClO_4 ^{55,56}, Li^+ , Na^+ , K^+ , Mg^{++} and Ba^{++} , NaI ,⁵⁷ NaSCN ⁵⁷, $\text{Poly}(2\text{-sulfonethylmethacrylate-Li})$ ⁵⁸, CuSCN ⁵⁹ have been thoroughly investigated.

The PEO salt complexes are generally prepared by direct interaction in solution for soluble systems or by immersion method, soaking the network cross-linked PEO in the appropriate salt solution⁵³⁻⁵⁸. Besides PEO,

poly(propylene)oxide, poly(ethylene)succinate, poly(epichlorohydrin), poly(ethylene terephthalate)⁶¹ and poly(ethylene imine) have also been explored as base polymers for solid electrolytes⁶⁰. Poly(ethylene imine) (PEI) is prepared by the ring-opening polymerization of 2-methyloxazoline. Solid solutions of PEI and NaI are obtained by dissolving both in acetonitrile (80°C) followed by cooling to room temperature and solvent evaporation in vacuo. Polyethyleneimine-NaCF₃SO₃ complexes have also been explored⁶².

Phosphate-ester cross-linked poly(ethylene glycols)⁶³ are obtained from the condensation of glycols with POCl₃. Partition of Li-trifluoromethanesulfonate-LiCF₃SO₃ between acetone solution and the polymer gel results in the formation of the electrolyte salt complexes⁶³.

Ti and Zr containing polytetramethylene oxide (PTMO) ceramic hybrid materials have lately been prepared by a sol-gel technique^{64,65}. Trialkoxy silane capped organic oligomers (PTMO or polyarylene ether sulfones) backbones with titanium isopropoxide or Zr-(n-propoxide) are used in this process.

Metal porphorines

Polymer-bound metalloporphorines are receiving considerable attention because of their various desirable properties. They are available by polymerization of vinyl group-containing porphorine or by immobilization of suitable porphorines on reactive polymers. The later method has the obvious advantage that complicated preparations are avoided. Some of the frequently used system in this regard are macroreticular resins in which porphorin moieties are monomolecularly dispersed. Hasegawa et al⁶⁶, Yamakita and Hayakawa⁶⁷ avoided the use of macroreticular resins by graft copolymerizing Cl-Me-Styrene onto porous polyolefins and subsequently making ester linkages between Cl-Me groups and the carboxyl groups of metalloporphorins. Some typical systems are 4-Cl-methyl styrene + N-vinyl pyrrolidone and their metal derivatives through radical copolymerization of styrene with Fe(II) or Fe(III) protoporphorins⁶⁸, and Cl-methylated polystyrene bound with combined Zn-complexes of a phthalocyanine⁶⁹ and a porphorin moiety⁶⁹.

A water insoluble homopolymer⁷⁰ of a vinyl monomer containing the pendant tetraphenyl porphorin and 4-vinyl

tetraphenyl porphorin have been synthesized by radical polymerization and subsequently complexed with manganese(III). The same group of workers also prepared water soluble anionic polymers by copolymerization of 4-vinyl tetraphenyl porphorine and sodium 4-styrene sulphonate and cationic polymers by quarternization of the copolymer of vinyl tetraphenyl porphorin and 4-vinyl pyridine.

Water-soluble polymer-bound porphorins have also been prepared by the reaction of poly(methacrylic acid) and poly(N-vinyl pyrrolidone-co-methacrylic acid) with the low-molecular weight substituted Zn complexes: tetraphenylporphorin, phthalocyanins and naphthocyanins^{71,72}. These reactions are conveniently performed by dissolving the base polymers in DMF/acetonitrile and subsequently activating the CO₂H groups by addition of triphenylphosphine, tetrachloromethane and triethylamine. This solution readily reacts with the appropriate porphorin moiety to form the charged polymer (containing residual unreacted COOH groups) or 'uncharged' ones (with the residual COOH groups being converted into methylester with diazomethane). Positively charged water-soluble styrene

based polymer bound porphorins have also been prepared through the reaction of poly(chloromethyl styrene) with low molecular weight porphorins in presence of triethylamine⁷².

Metal phthalocyanine-imide polymers

Poly(metal phthalocyanine)imide copolymers are produced from the reaction of metal(II)4,4',4'',4'''-phthalocyanine tetramine(Cu, Co, Ni)diamines:4-phenylene, 4,4'-bis(4-aminophenyl)methane, 9,9'-bis(4-aminophenyl)fluorene) and 1,2,4,5-benzene tetracarboxylic dianhydride⁷³.

A novel synthetic approach to preparation of conductive polyphthalocynins is due to Lin and Dudek who employed thermal cyclization of poly(Cu(II),2,3,9,10,16,17,23,24-octacyano) phthalocyanine to obtain a conducting system with extended π -conjugation⁷⁴.

Shirai et al⁷⁵ also synthesized a novel class of polyimides containing M(II) phthalocyanine rings by solution condensation in N-Me-2-pyrrolidone of M(II) [2,9 or 10,2,16 or 17-bis(3,4-dicarboxy benzoyl)] phthalocyanine dianhydride with 2,6-diaminopyridine followed by thermal imidation⁷⁵.

Recently polymeric phthalocyanines containing peripheral carboxyl groups have also been converted into corresponding environmentally stable electrically conductive polyimides⁷⁶.

Wohrle et al⁶⁹ reported the synthesis of covalently bound phthalocyanine moieties to chloromethylated polystyrene polymethacrylic acid poly(N-vinylpyrrolidone-co-methacrylic acid)⁷¹.

Crown ethers

Poly(crown ethers) have received a great deal of attention in view of their cation binding selectivity. They are expected to show a higher binding ability for large alkali metal cations than the monomeric analogues due to a cooperative action of two neighbouring crown ether moieties in the polymer chain. The cooperative action can be affected by the relative position of the neighbouring crown-ether moieties attached to the polymer backbone^{77,78}. In a novel synthetic procedure, Shirai et al⁷⁸ have developed a facile way to fix the relative position of two crown ether moieties by photodimerization of cinnamic acid moieties introduced in the monomer. Thus, a benzo 15-Crown-5 having ether acryloyl or

vinyllic functionality undergo crosslinking through photodimerisation through the unsaturated moieties.

Crown-ether network polymers have also been prepared by adding to a slurry of NaH in THF, an equimolar amount of the appropriate hydroxy containing crown-ethers followed by the addition of chloromethylated cross-linked polystyrene. Binding of Na, K, Cs picrates and of sodium tetraphenyl-borate to the immobilized crown-ether is achieved under simple conditions⁷⁹.

A new class of polyamides containing dibenzo 18-crown-6-moieties and alkaline units in the main chain shows⁸⁰ varying complexing capabilities with 4-toluene sulfonates of Rb⁺, K⁺, Na⁺ and potassium salts of CH₃C₆H₄SO₃⁻, SCN⁻, I⁻, Br⁻.

Schiff's base chelates

Polymer bound Schiff's bases are receiving increasing attention, as these materials are expected to combine the selective properties of low molecular weight Schiff's base chelates with the advantage of polymer immobilization. Wohrle et al⁷ synthesized a copolymer of 2-butyylimino-4-vinylphenol with styrene to prepare N,N,O-chelates⁷.

N-alkylation of low molecular weight N_3O_2 -ligands with chloromethylated polystyrene results in immobilized Schiff's base structures⁸¹. Co(II), Mn(II) and Fe(II) complexes of these bases have been investigated⁸¹.

Metal-containing liquid-crystal polymers

A Cu^{2+} containing linear polymer⁸² exhibiting smectogenic behaviour is obtained by a polycondensation technique (Fig.1.4). A homologous set of polycondensates of 4,4'-[1,12 dodecanediyl bis(oxy)] bis benzoic acid with bis[N-[[2,4 dihydrophenyl]methylene]-alkylamino] Cu(II) exhibits monotropic liquid crystalline behaviour with 4-13 carbon atoms in the alkylamino group⁸³.

Metal-Containing Plasma Polymers

The introduction of metals into plasma polymers has been the subject of some research during recent years. Basically, three methods have been used (a) Plasma polymerization of organometallic compounds^{84,85} (b) Concomitant etching or sputtering of metals⁸⁶ and (c) Evaporation of metals into a plasma polymerization system⁸⁷. Munro et al^{88,89} incorporated mercury into plasma-polymerized perfluorobenzene by mixing Hg-vapor with the perfluorobenzene prior to entering them in the

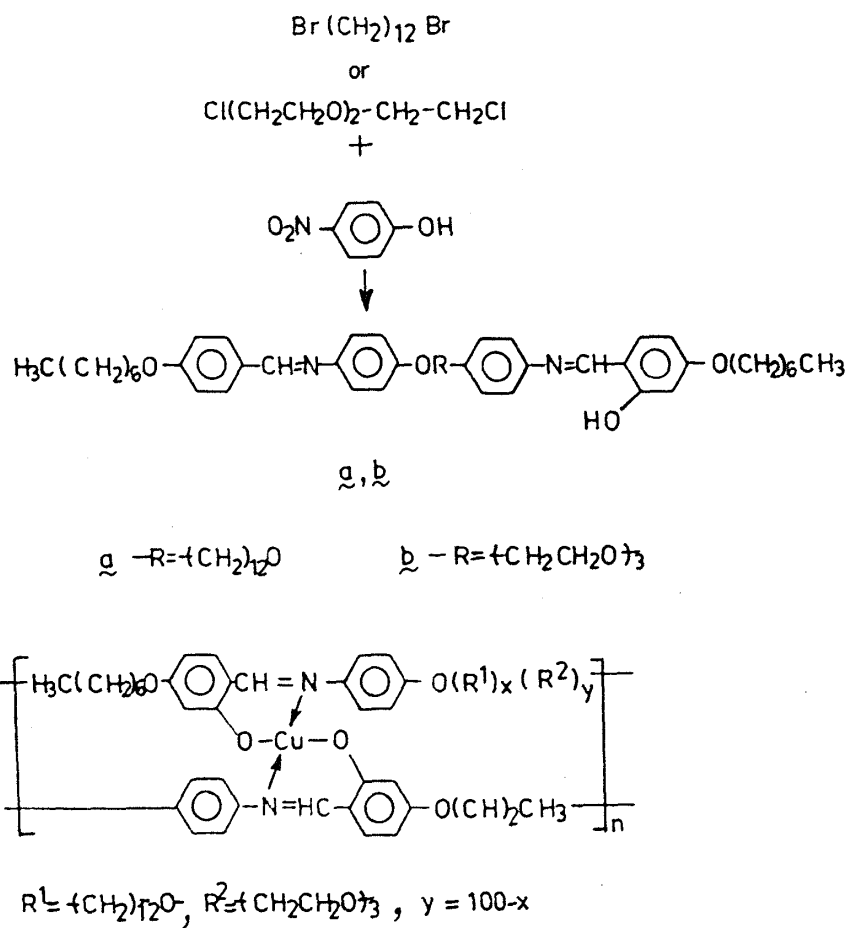


Figure 1.4 Metal containing liquid crystal polymers

plasma reactor. Munro et al also prepared^{88,89} plasma polymers of ferrocene, vinylferrocene and dimethylamino-methyl ferrocene.

Doping

Direct incorporation of metal ion moieties in a polymer chain by doping is a frequently used method. Mostly, acetylene polymers⁹⁰⁻⁹³, poly(arylene vinylenes)⁹⁴, poly(phenylene sulfides)⁹⁵ with systems of conjugated π -electrons are doped directly with numerous metal salts and elements via charge transfer complex formation. Various metal salts used include, PtCl_4 , $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, LiClO_4 , FeCl_3 , Ga, In, TiCl_3 and organo Li compounds.

Electrochemical doping of insulating polymers has been attempted for polyacetylene, polypyrrole, poly-N-vinyl carbazole and phthalocyaninato-poly-siloxane. Significantly, Shirota et al⁹⁶, claim to have achieved the first synthesis of electrically conducting poly(vinyl ferrocene) by the method of electrochemical deposition (ECD)⁹⁶. This is based on the insolubilization of doped polymers from a solution of neutral polymers. A typical procedure applied⁹⁶ for polyvinyl ferrocene is to

dissolve the polymer in dichloromethane and oxidize it anodically with Ag/Ag^+ reference electrode under selective conditions. The modified polymer⁹⁶ is a partially oxidized mixed valence salt containing ferrocene and ferrocenium ion pendant groups with ClO_4^- as the counter anion.

A few systems obtained by ECD method comprise polyacetylene tetrachloroferrate⁹² $[\text{CH}(\text{FeCl}_4)_y]_x$ and tetrachloroaluminate $[\text{CH}(\text{AlCl}_4)_x]$, Li^+ doping (LiClO_4 in propylene carbonate)⁹¹ or $[(\text{CH})_x(\text{SbF}_6)_y]_n$ (anodic oxidation in a solution of $[\text{CH}_3(\text{CH}_2)_3]_4 \text{N}^+ \text{SbF}_6^-$ in dry CH_2Cl_2)⁹².

Mechanochemical Synthesis

Mechanochemical synthesis of some macromolecular complexes of Mn with polyamides and polyesters have been achieved. Simionescu et al⁹⁷ reported the ultrasonic mechanochemical condensation of poly(ethylene terephthalate, PET) with ethylenediamine as ligand for V^{3+} , and of poly(ϵ -caprolactam) as ligand for Mn^{2+} , by vibratory milling.

A compression moulding technique⁹⁸ has been used to prepare composites of polystyrene with layered perovskites $C_{12}Mn$; polystyrene powder ($M_n=145\ 000$) and finely powdered $C_{12}Mn$ (average particle size $150\ \mu m$) are dry blended and subsequently compression moulded at $160^\circ C$ and a pressure of $50\ Kg/cm^2$.

1.2.2 EVALUATION OF METAL-CONTAINING POLYMERS

One of the obvious objectives of metal ion incorporation into polymers is to modify the essential bulk properties of these polymers with regard to miscellaneous end-uses. To this end however, structure-property correlations although useful, are difficult to achieve, particularly when high polymer networks are involved. This section will highlight the available information as to how metal-ion incorporation can affect thermal stability, electrical and other useful properties of the polymer systems of which they are part.

Thermal Stability

Acrylic Polymers.

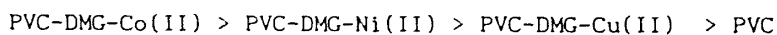
Burrows et al⁹⁹ showed by the 'Integral Procedural Decomposition Temperature' (IPDT) method that for main

group metal ions - the stabilizing effect in regard to polyacrylamide is inversely proportional to the radius of the metal ion reemphasizing that the strength of the complex between the ion and the polymer is of importance in deciding the stability.

Polyvinyl Chloride

Divalent metal ions - as long chain alkylcarboxylates of Cd(II), Ba(II), Zn(II) have been reported to stabilize PVC against dehydrochlorination¹⁰⁰.

Biswas and Moitra¹⁰⁶ recently established that the '3d' metal ions incorporated in PVC-DMG-complex enhance the thermal stability of PVC in the order:



which is the same order as the 'crystal field stabilization energy' (CFSE) of the individual metal complexes.

Styrene Polymers

Polystyrene-divinylbenzene immobilized 3d metal dipyriddy complexes also exhibit enhanced thermal stability as in the case with the polyacrylics. Biswas

and Mukherjee¹⁸ more recently reported the enhancement of thermal stability of 3d metal ion loaded PS-DVB-DPA-M(II) complexes in the order: -Co(II) < -Fe(III) < -Cu(II). However, the T_gs of these polymers as determined by a thermo mechanical analyzer, do not reveal any major variation from each other: PS-DVB (123°C), PS-DVB-DPA-Fe(II) (123°C), PS-DVB-DPA-Co(II) (129°C), PS-DVB-DPA-Cu(II) (120°C).

Polyethylene Oxide and Related Polymers.

Wright reported that NH₄⁺, K⁺ and Na⁺ thiocyanates from crystalline complexes with PEO whose melting temperatures increase with decreasing cation size (T_m=343, 373 and 468 K with NH₄⁺, K⁺, Na⁺ respectively)⁵⁷. The complexation is believed⁵⁷ to involve coordination of ethereal oxygen atoms to the cation in macrocyclic polyether complexes. Complexation with NaSCN of a poly(ethylene-oxide-b-isoprene-b-ethylene oxide)¹⁰¹ occurs selectively with PEO end blocks and yields a semicrystalline thermoplastic elastomer melting at 450 K, 90 K lower than that of the complexed block polymer. The

* This data originated out of the research submitted in this thesis and will be discussed in due course in appropriate details.

heterogeneous nuclei are segregated in a few isolated crystallizable microdomains and hence cannot contribute to the nucleation of the greater part of the crystallizable component.

DSC traces of polyethyleneimine complexed with NaI also give evidence⁶⁰ for strong interaction of the salt with the polymer by a decrease in crystallinity of the polymer and ultimate loss of crystallinity of the polymer at molar ratio (NaI/CH₂CH₂NH) of 0.15. At higher concentrations, a new endotherm manifests at 150°C due to the specific crystalline complex between NaI and PEO. DTA studies of PEO-NaI and PEO-NaSCN complexes further reveal that melting temperature of the lamellar phase (crystalline) is independent of the nature of the anion⁵⁷.

Poly-condensates.

Taylor et al observed¹⁰² that high temperature adhesive properties of the polyimide derived from 3,3',4,4'-tetracarboxybenzophenone dianhydride (BTDA) and 3,3'-diaminobenzophenone (DAB) are significantly enhanced by doping with Al(AcAc)₃. The polyimide (DTDA+DAB) similarly¹⁰² yields on doping with

$[(n\text{-Bu})_3\text{PCuI}]_4$ a flexible thin film. Copper increases the softening temperature of the polyimide in air with optimization being reached around 2.6% Cu. Cu-weight percent upto 2.6% has little effect on the decomposition temperature of the polymers¹⁰². The effect of Cu(II) dopants as 1,3-diketonates and Schiff's base derivatives on imidization of ETDA+DAB - is to induce a higher apparent T_g and low-temperature weight losses (Cu(I) dopant > Cu(II)) even though, total decomposition occurs at a higher temperature in Cu(I) than in Cu(II) system. Taylor et al [43] also confirmed that in situ co-deposition of Co and Li salts in condensation polyimides results in lower stability than the same obtained by Li/Co ion deposition⁴³ - both, however, causing lower stabilities in the parent polyimide. This may be due to (i) Co/Li may either act synergistically to reduce the stability or (ii) higher overall ionic content in the codoped sample vs the singly doped film may be the factor.

Mechanochemically introduced V^{3+} and Mn^{2+} complexes of poly(ethylene terephthalate) also exhibit enhanced thermal stability of the base polymer -an observation in line with the usual expectation⁹⁷.

Biswas and Mazumdar^{50,51} reported a similar enhancement of thermal stability on metal ion incorporation for the polycondensate PMDA-DP/DPA/M, with the following features of interest: (i) With a typical metal ion incorporated in either PMDA-DP or PMDA-DPA, initial decomposition temperature of the metal-loaded polymers does not change significantly: PMDA-DP (238°C), PMDA-DPA (235°C), PMDA-DP-Fe(III) (280°C), PMDA-DPA-Fe(III) (290°C), PMDA-DPA-Cu(II) (265°C), PMDA-DP-Ni(II) (265°C), PMDA-DP-Ni(II) (263°C), PMDA-DP-Ni(II) (280°C). (ii) With either PMDA-DP or -DPA, the effect of different metal ions on the stability is in the order $Fe^{3+} > Ni^{2+} > Cu^{2+}$ (upto 4% decomposition) in the DPA complex, and upto 25% in the DP complex. (iii) Beyond this temperature, the order in stability becomes same in either system: $Fe^{3+} > Cu^{2+} > Ni^{2+}$.

Phthalocyanine Polymers

Phthalocyanin-imide polymers show an initial decomposition temperature $> 500^{\circ}C$ both in air and inert atmosphere (Co, Ni, Cu, Zn). As expected, an increase in the concentration of metal phthalocyanin in the copolymer increases the thermal stability⁷⁴. Poly(Cu



2,3,9,10,16,17,23,24-octacyanophthalocyanin) represents an unique polymer showing enhanced thermal stability (1.2% wt. loss at 585°C and 1.5% wt. loss at 625°C, 21.6% at 800°C) in He atmosphere; rapid oxidation takes place on heating above 560°C (9% wt. loss at 585°C)¹⁰³. The enhanced stability of this material is different from that of monomeric metal phthalocyanin compounds which sublime and loose most of their weight around 600°C¹⁰³.

Schiff's Bases

Coordination polymers of Ag(I), Cu(II), Zn(II) and Ti(IV) exhibit improved thermal stability in the order Cu < Ag < Ti < Zn¹⁰⁴. Replacement of a benzyl by a phenyl group as substituent at the amino group of the ligand also enhances the stability.

Electrical Properties: Conductivity and Dielectric Characteristics

Acrylic Polymers

PMMA films doped with 1.7% wt. FeCl₃ exhibit¹⁰⁵ a characteristic log conductivity vs 1/T plot comprising two segments separated by a glass-rubber transition temperature ($E_g = 25$ kcal/mol; $E_p = 16.3$ kcal/mol

respectively). For the doped system however, three segments manifest. Activation energies for the 1st and 3rd segments decrease with increasing FeCl_3 concentration implying that FeCl_3 enters the matrix through attachment via the ester group and thereby assists the formation of continuous conduction paths in the polymer matrix. SEM and electron microprobe analysis endorse that the FeCl_3 doped PMMA contains three phases α, β and γ ; the β phase being the halide-rich phase distributed in the least halide containing phase (α) and the highest halide containing γ phase. Characteristically E_2 (β phase) increases upto 4% FeCl_3 , implying increase in charge carrier density and falls subsequently at higher FeCl_3 concentration.

Polyvinyl Chloride

Biswas and Moitra¹⁰⁶ observed substantial increase in conductivity for metal modified PVC-DMG-M(II) complexes. Interestingly, conductivities appreciably increase relative to PVC in the order: PVC < PVC-DMG-Cu(II) < PVC-DMG-Ni(II) < PVC-DMG-Co(II) (Table 1.1). The enhancement in the conductivity is readily ascribable to the varying extents of charge transfer between the 3d metal ion centers and the electron-rich

Table 1.1 Electrical conductivity of PVC-DMG-M(II) [106]

Polymer	Diameter (mm)	Thickness (mm)	Voltage (V)	Current (A)	Electrical conductivity ($\Omega^{-1}\text{cm}^{-1}$)
PVC(pure)	11.6	1.75	20	0.14×10^{-8}	1.68×10^{-11}
PVC-DMG-Cu	11.8	1.85	20	6.1×10^{-8}	5.44×10^{-10}
PVC-DMG-Ni	11.65	1.55	20	0.6×10^{-6}	4.36×10^{-9}
PVC-DMG-Co	11.75	2.00	20	9.0×10^{-4}	8.30×10^{-6}

heteroatoms in DMG. Apparently, ease of such charge transfer will depend upon the availability of '3d' vacant orbitals which follows the order: $\text{Co}^{2+} (3d^7) > \text{Ni}^{2+} (3d^8) > \text{Cu}^{2+} (3d^9)$.

Dielectric characteristics. At low frequency (10 kHz-100 Hz) the dielectric constant obey the trend $\text{PVC} < \text{PVC-DMG-Cu(II)} < \text{PVC-DMG-Ni(II)} < \text{PVC-DMG-Co(II)}$. The dielectric constant fall monotonously with the applied frequency. The dielectric loss ($\tan \delta$) parameter also falls steadily with the applied frequency. However, PVC-DMG-Co(II) exhibits a comparatively large fall in $\tan \delta$ from 2.5 to 0.2 in the frequency range (100 KHz-10MHz), while PVC-DMG-Ni(II) shows a smooth fall in $\tan \delta$ from 0.1 to 0.05 in the same frequency range. The introduction of polar groups in PVC will cause them to orient when placed in an electric field. If these groups are flexibly attached to the polymer chain, they will orient easily and rapidly. If the polymer is rigid, and the polar groups are rigidly attached, they will orient slowly with difficulty. In an alternating electric field, the polar groups in the polymer will orient and give high permittivity only when the frequency of alteration is low enough to permit motion and orientation of these groups.

With increasing frequency in the alteration of electric field, the polar groups will be able to orient less and less rapidly and at still higher frequencies, they will be able to orient hardly at all. As a result the polymer will exhibit low permittivity. As for the broad nature of loss tangent parameter, it seems that loss of electric energy by conversion to thermal energy is too small to be detected at low frequency. It shows up only at some intermediate frequency in the transition region, where the polar groups are able to orient at the rate and frequency of alteration in the electric field.

Poly(vinyl alcohol)

Dielectric measurements were made with samples of poly(vinyl alcohol)¹⁰⁷ doped with hydrous cobalt chloride (5-30%). Dielectric measurements were performed at various temperatures and frequencies in order to investigate the effect of cobalt chloride on relative permittivity and dielectric loss factor ($\tan \delta$) of the polymer.

While pure poly(vinyl alcohol) showed dielectric constant values typical of polar dielectrics, poly(vinyl alcohol) doped with >10% CoCl_2 behaved as a nonpolar

dielectric in the temperature range 40-70°C. The $\tan \delta$ values suggested that the activation energy for dipole segmental and dipole group orientation increases with CoCl_2 addition.

Styrene Polymers.

While polystyrene shows¹⁰⁸ a room temperature dc conductivity in the order $3 \times 10^{-20} \text{ Ohm}^{-1} \text{ cm}^{-1}$, the complexes of polystyrene with metallic salts, PS- AlCuCl_4 , PS- AgAlCl_4 , PS- AlCl_3 , PS- CuCl and PS- AgClO_4 exhibit values in the order $10^{-11} - 10^{-16}$. The enhancement in the conductivities arises from larger extents of charge-transfer interaction between aromatic nucleus of polystyrene and the complexing metal salts, simple salts (AgClO_4) exhibiting lower values than the double-salts.

Volume resistivity⁹⁸ of polystyrene compression moulded with organometallic $[(n\text{-C}_{12}\text{H}_{25}\text{NH}_3)_2\text{MnCl}_4]$ layered perovskites fall in the range $10^{10} - 10^{18} \text{ ohm}^{-1} \text{ cm}^{-1}$ depending upon (i) the percentage of the filler, the effect being more pronounced at 80°C than at 30°C and (ii) orientation of the layers in the compression moulded structure. Such anisotropy in conductivity is also known for nylon 6-6 and other systems⁹⁸.

Polyacetylenes

Numerous attempts have been made to enhance electrical conductivity of modified polydiacetylenes by doping. Both 'n' and 'p' type doping has been studied. Organo-lithium compounds have been widely used as dopants. Salts of transition metal ions WCl_3 , $MoCl_5$, $H_2IrCl_6 \cdot 6H_2O$, $FeCl_3$, are receiving increased attention as dopants for polyacetylenes. Table 1.2 collects some significant data to compare the conductivities in polyacetylenes in the presence of metallic dopants. A mechanistic understanding of doping in polyacetylenes has involved a variety of surface/structure characterization techniques like X-ray diffraction, scanning electron micrography⁹³, transmission electron microscopy (TEM)⁹³, Raman and X-ray photoelectron spectroscopy⁹³ and casting microprobe analysis¹⁰⁹. X-ray photoelectron spectroscopy(XPS) results show that upon doping, oxidation of polyacetylene chain is accompanied by partial reduction of Pt^{4+} to Pt^{2+} , the dopant anion being $PtCl_6^{2-}$ for both $PtCl_4$ and $H_2PtCl_6 \cdot 6H_2O$, doped polyacetylene⁹⁰. SEM studies of metal halide doped polyacetylenes have confirmed fibrillar nature of $(CH)_x$ films and decrease of porosity

Table 1.2 Conductivities in polyacetylenes in presence of metallic dopants

Polymer	Dopant	Conductivity ($\Omega^{-1}\text{cm}^{-1}$)	Ref.
Polyacetylene	Li-benzophenone	100	91
-do-	PtCl_4	134	90
-do-	$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	12	90
-do-	RhCl_3	6×10^{-4}	90
-do-	CuCl_2	1.8×10^{-3}	90
-do-	MoCl_5	200	109
-do-	WCl_6	200	109

due to swelling of fibrils⁹³. Interestingly, it has been endorsed by EPR, IR/visible and conductivity measurements that by doping with Li-benzophenone⁹¹ cis-rich(CH)_x films can reach the metallic level, and Raman spectroscopy confirms that doping is followed by isomerization of (CH)_x from cis to trans structure⁹¹.

Phthalocyanine Polymers

As mentioned earlier¹⁰³, thermal cyclization of poly(Cu,2,3,9,10,16,17,23,24-octacyanophthalocyanine) induces a dramatic improvement of the conductivities. The polymer, cyclized at 203°C, has a room temperature conductivity of ca. 6.7×10^{-6} (Ohm⁻¹cm⁻¹) in air; cyclized at 400°C the conductivity is enhanced 3 times which is claimed to be due to elimination of impurities. At 600-700°C, large extensive cyclization (both inter and intramolecular) leads to highly conjugated structure; cyclized at 900°C, the polymer exhibits conductivity in the range 4.6-8(ohm⁻¹ cm⁻¹) with only ca. 21.9% weight-loss.

Similarly, in another such example the polymeric copper phthalocyanine containing peripheral carbonyl groups⁷² increased its conductivity from 10^{-9} Ohm⁻¹ cm⁻¹

to $\approx 2.25 \text{ ohm}^{-1} \text{ cm}^{-1}$. It was also observed that during heat treatment, the polymer lost weight in a linear fashion.

Polycondensates

Miscellaneous copolycondensates with ligands as comonomers bind metal ions to produce conducting materials. Table 1.3 collects a few available data on such systems.

Dielectric Characteristics

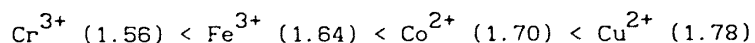
Dielectric studies carried on PMDA-DP and PMDA-DPA by Biswas and Majumdar⁵¹ revealed the following typical features: (i) The dielectric values for PMDA-DP and PMDA-DPA complexes fall between 7-8, which is in the range expected for polar polymers. Changing the frequency from 10^3 to 10^7 Hz alters the dielectric values by only 3% (ii) On incorporation of metal ions in these complexes, the dielectric constant values are slightly enhanced in the above frequency range. (iii) At a particular frequency (ca. 10 KHz) the dielectric constant values for the PMDA-DP-M complexes depend slightly on the nature of the metal ion in the order:

Table 1.3 Conductivities in some polycondensates

Polycondensate	Metal ions	Conductivity ($\Omega^{-1}\text{cm}^{-1}$)	Ref.
Poly(metal tetra- thiooxalates)	$\text{Cu}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Pd}$	1-20 Stable on exposure to ambient environments for several months	110
Pyromellitic dianhydride- bipyridyl/ bipyridylamine	$\text{Cu}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Fe}^{\text{II}}$ $\text{Fe}^{\text{III}}, \text{Cr}^{\text{III}}$	1.7×10^{-8} -5×10^{-10} depending upon metal ion	50,51
Polyarylenevinylenes	AsF_5 doped	1.8×10^{-7} depending on substitutens	94

PMDA-DP-Cr(III)(9.2) > PMDA-DP-Fe(III) (8.7)
> PMDA-DP-Cu(II) (8.1)
> PMDA-DP (8.0)

A similar trend is also noted for the PMDA-DPA-M complexes. (iv) These polymers exhibit rather low dielectric loss ($\tan \delta = 1-4 \times 10^{-2}$ at 10 KHz which however is strongly dependent on the applied frequency. Thus, a broad relaxation pattern is typically observed even though the dielectric constant is not drastically changed. The observed order in dielectric constant with the 3d-metal ions is significantly also the order in which the electronegativity of the metal ion changes:



This implies that the electronegativity difference between nitrogen and the metal decreases in the series leading to a decreased extent of dielectric polarization as actually observed. The frequency dependence of the $\tan \delta$ values in these complexes is marked. Evidently, the metal complexes possess a rigid structure where dipoles do not find sufficient time for alteration resulting thereby in a broad dielectric relaxation.

PEO and Related Systems

High ionic conductivities have been characteristically associated with polymer-alkali metal complexes, which are receiving a great deal of research attention as electrolytes for solid state batteries. LiClO_4 dispersed homogeneously in cross-linked (β -cyanoethyl methylsiloxane)poly (β -cyanoethyl methylsiloxane-co-dimethylsiloxane) shows a network film conducting in the order of $10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature¹¹¹.

In alkali metal salt-PEO complexes^{53,55,56}, the alkali metal ions are situated in an electron-rich environment surrounded by ethereal oxygen of PEO and the charge-carriers are the cations and the anions. In Li-thiocyanate-PEO complex the transport number of Li is 0.5, as determined by several workers. Ward et al.⁵⁸ have developed two simple procedures to achieve Li^+ transport numbers close to unity: (i) by incorporating anion as part of a polymer chain when their transport number will be zero and the cations will be the major charge carriers. This is achieved⁵⁸ by producing blends of PEO and Li salts of the ionic polymer and (ii) by inhibiting

Table 1.4 Conductivities^a of polyethylenic and allied systems

System	Mol. wt.	Complexed with	Conductivities ohm ⁻¹ cm ⁻¹	Temp. K	Ref.
PEO	600	NaI(1:6)	10 ⁻³ -10 ⁻⁶	298-450	57
	10000	NaI(1:4)	10 ⁻³ -10 ⁻⁸	298-450	57
	600000	NaI(1:3;2)	10 ⁻⁵ -10 ⁻⁹	298-450	57
	10000	NaSCN	10 ⁻³ -10 ⁻⁹	298-450	57
PEO	400	LiBF ₄ (s) ^b	10 ⁻³ -10 ⁻⁵	298-450	53
	400	LiBF ₄ (us) ^c	3.1×10 ⁻⁴ -3.1×10 ⁻⁵	298-450	53
	5×10 ⁶	LiBF ₄	10 ⁻⁵ -10 ⁻⁷	298-450	53
	5×10 ⁶	LiCF ₃ SO ₃	10 ⁻⁵ -10 ⁻⁷	298-450	53
PEO	4×10 ⁶	CH ₃ COOLi ^d			
		O/Li ⁺ = 4	3.16×10 ⁻⁴ -10 ⁻⁹	298-420	58
		O/Li ⁺ = 9	10 ⁻⁴ -10 ⁻⁹	298-420	58
		O/Li ⁺ = 18	10 ⁻⁴ -10 ⁻⁸	194-420	58
	SO ₃ SO ₃ Li				
	O/Li ⁺ = 9	10 ⁻³ -10 ⁻⁷	298-420	58	
	O/Li ⁺ = 18	10 ⁻³ -10 ⁻⁷	298-420	58	
	CF ₃ COLi	10 ⁻³ -10 ⁻⁹	298-420	58	
	CF ₃ CF ₂ COLi	10 ⁻³ -10 ⁻⁸	298-420	58	
	CF ₃ CF ₂ CF ₂ COOLi	10 ⁻⁴ -10 ⁻⁹	298-420	58	
LiHFG ^e	10 ⁻⁴ -10 ⁻¹⁰	298-420	58		
PEO	5×10 ⁶	Na ⁺ with TCNQ ^f	10 ⁻² -10 ^{-4g}	298-420	
PEO (cross- linked)	3000	LiClO ₄			
		LiClO ₄ /EO unit = 0.2	10 ⁻² -10 ⁻⁹	253-373	56
PEO(linear)	3000	LiClO ₄ /EO unit = 0.05	10 ⁻⁸ -10 ⁻¹¹	253-373	56

contd..

Table 1.4 (contd)

System	Mol. wt.	Complexed with	Conductivities $\text{ohm}^{-1}\text{cm}^{-1}$	Temp. K	Ref.
Phosphate ester cross-linked	400	LiCF_3SO_3			
Polyethylene glycols		$\text{O/Li}^+ = 27.6$	5.2×10^{-6}	293	63
		$\text{O/Li} = 13.7$	2.5×10^{-6}	293	63
Poly (ethylenimine) (PEI)	2×10^5	$[(\text{EI})_x \text{NaCF}_3\text{SO}_3]_n$			
		$x = 4$	5.6×10^{-8}	314	62
			1.2×10^{-5}	367	62
		$x = 5$	2.4×10^{-7}	314	62
			5.4×10^{-5}	366	62
		$x = 6$	2.4×10^{-7}	314	62
			5.4×10^{-5}	366	62
PEI	2000	NaI 0.3 mol. ratio	$10^{-3} - 10^{-8}$	340-450	60
PEO*	400	LiClO_4	$10^{-4} - 10^{-7}$	20-50%	55

^aac Conductivities are reported if not mentioned otherwise

^bSaturated concentrations (s)

^cUnsaturated concentrations (us)

^dSalt concentrations are quoted as the ratio of the number of moles of oxygen atoms in PEO to the number of moles of Li^+ ions (O/Li^+)

^eDilithium hexafluoroglutarate $\text{LiOOC}(\text{CF}_2)\text{COOLi}$ (LiHFG).

^fTetracyanoquinodimethane radical anions (TCNQ).

^gdc Conductivity reported

* Conductivity measured as a percentage(%) of epoxyglycidylether of bisphenol A.

the mobility of the anion by using a Li salt of dibasic acid, dilithium hexafluoroglutarate.

More recently, Tsuchida et al.¹¹² achieved a Na⁺ ionic conductivity $1 \times 10^{-6} \text{ Ohm}^{-1} \text{ cm}^{-1}$ in a composite film made from Nafion (perfluorosulfonate ions) and diendo-acetylated polyoxy ethylene, due apparently to enhanced dissociation of the sodium perfluoro sulfonated groups in the composite matrix.

Table 1.4 summarizes the conductivity ranges reported for various PEO-salt systems and suggests that the conductivities depend on (a) polymer molecular weight (b) polymer-salt ratio and temperature. As expected, the polymer salt ratio is one of the most significant factors.

1.3 OBJECT AND SCOPE OF THE PRESENT INVESTIGATION

The survey of the present status of research on metal containing polymers highlighted briefly in the preceeding section endorses that there is a global interest in the synthesis and evaluation of metal containing polymers. The survey further indicates that more concerted research is warranted on

structure-property correlation in metal containing polymers.

The work to be highlighted in the present thesis is essentially concerned with this latter aspect. The research was undertaken with the following specific objectives in view:

1. To select a particular preformed polymer matrix, PS-DVB in this case and anchor on it a number of 3d-metal-ligand complexes.
2. To prepare a copolycondensate with metal-ligand complex in the main chain by polycondensation between bifunctional anhydrides, pyromellitic dianhydride and trimellitic anhydride and 3d-metal-ligand, (1,10-phenanthroline) complex.
3. To identify from studies on (1) and (2) any distinctive features in the bulk properties of the polymers that may result from two different modes of metal complex incorporation, i.e. metal complexes pendant on preformed polymer and those lying in the main chain backbone.

4. (a) To introduce structural variations in these systems by varying the metal ion in either systems keeping the ligand fixed. In view of the distinctive properties of transitional elements Cu^{2+} , Co^{2+} , Fe^{3+} and Fe^{2+} of the first transition series were chosen for ligand complexation in either system. and (b) by varying the nature of the ligand moiety keeping the metal ion fixed (2,2'-dipyridyl and 1,10-phenanthroline) with Cu(II).
5. To structurally characterize the various metal complex incorporated polymer systems by elemental analyses, UV and IR spectroscopy; to study morphology by XRD analysis and surface characteristics by scanning electron micrography; and to ascertain the chemical characteristics of the incorporated metal ions by X-ray Photoelectron Spectroscopy (XPS) studies.
6. To evaluate the thermogravimetric stability and identify the characteristic thermodegradation processes by DTA, IR and XPS studies in respect of (a) PS-DVB-DPA-M ($M = \text{Cu}^{2+}$, Co^{2+} , Fe^{3+}), (b) 3d-metal based anhydride copolycondensates with ligands 1,10 phenanthroline and 2-2' DP/DPA (fixed M

Cu^{II}), with a fixed ligand (Phen) M = Cu^{II} and Fe^{III} and with a fixed 3d-M-Ligand aryng anhydride counterpart (TMA, PMDA), and finally to compare contrast, and rationalize the thermal stability features of all these systems in terms of structural, and other relevant parameters of the chemical moieties concerned.

7. To evaluate the dielectric properties ϵ' dielectric constant and $\tan \delta$ loss parameters of the copolycondensates and establish any correlation of these properties with the various structural parameters as (a) metal ions varying from Cu(II) to Fe(III) with ligand and anhydride fixed; (b) with a fixed M, the ligand varying from less polar 2,2' dipyridyl to more polar 1,10-phenanthroline and (c) the anhydride counterpart varying from pyromellitic dianhydride to trimellitic anhydride differing in steric and functionality characteristics.
8. To elucidate the dc conductivity and field dependent ac conductivity characteristics of the various copolycondensates and the metal derivatives thereof and examine their likely dependence on structural parameters of the various polycondensates.

9. To examine the polymerization initiating activity of these various '3d' metal ligand bearing polymer systems, with regard to some vinyl monomers.

Attempts were made to experimentally study in appropriate details, the various objectives outlined as above. The salient aspects of the experimental procedure adopted and the results achieved through these studies, vis-a-vis their rationalization and discussions are presented in this dissertation.

